Coulomb correlations do not fill the e'_g hole pockets in Na$_{0.3}$CoO$_2$

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There exists presently considerable debate over the question whether local Coulomb interactions can explain the absence of the small e'_g Fermi surface hole pockets in photoemission studies of Na$_{0.3}$CoO$_2$. By comparing dynamical mean field results for different single particle Hamiltonians and exact diagonalization as well as quantum Monte Carlo treatments, we show that, for realistic values of the Coulomb energy U and Hund exchange J, the e'_g pockets can be slightly enhanced or reduced compared to band structure predictions, but they do not disappear.

The Fermi surface of a material is one of its most fundamental properties. Usually, it can be understood, at least qualitatively, within density functional theory. It came as a surprise, therefore, when several angle-resolved photoemission (ARPES) studies on the intercalated layer compound Na$_{0.3}$CoO$_2$ [1] revealed a fundamentally different shape of the Fermi surface than predicted by local density approximation (LDA) band theory [2]. Recent bulk sensitive Shubnikov-de Haas data [3] also appear to be inconsistent with these calculations. On the other hand, the overall width of the Co 3d bands in the ARPES data was found to be only moderately reduced compared to the LDA value. Essentially, the partially filled Co 3d t_{2g} bands should give rise to a large a_g hole pocket centered around Γ, and six small hole pockets of e'_g character along the ΓK directions of the hexagonal Brillouin Zone. These e'_g pockets have not yet been observed in experimental work. Their role for the superconducting hydrated phase of Na$_{0.3}$CoO$_2$ is also a subject of intense investigations [4]. In view of the narrow width of the Co t_{2g} bands ($W \approx 1.5$ eV), one possible source of the discrepancy between ARPES and band theory might be the effect of intra-3d Co Coulomb interactions which, in principle, could enhance orbital polarization by leading to a charge transfer from a_g to e'_g subbands, and, eventually, to a shift of the e'_g bands below the Fermi level.

The influence of Coulomb interactions on the topology of the Fermi surface of Na$_{0.3}$CoO$_2$ has been investigated by several groups, using various theoretical methods and levels of approximation. Ishida et $al.$ [5] applied dynamical mean field theory (DMFT) [6] based on the multi-orbital quantum Monte Carlo (QMC) method, together with a single-particle Hamiltonian derived from an accurate tight-binding fit of the t_{2g} bands to the linearized augmented plane wave (LAPW) band structure. The result of this work was that, for Coulomb energies $U \approx 3.0 \ldots 3.5$ eV and exchange $J = U/4$, the e'_g hole pockets were slightly enlarged compared to the LDA Fermi surface, in contrast to the ARPES data. The width of the t_{2g} bands, however, was found to be reduced to about 1 eV, in approximate agreement with ARPES. To avoid sign problems, only Ising-like exchange terms were included in the QMC calculation. It was also shown that an LDA+U [7] treatment can lead to enlarged or reduced e'_g hole pockets, depending on whether U is smaller or larger than 5J, respectively.

At the same time, Zhou et $al.$ [8] investigated this problem within the Gutzwiller approach in the large U, $J = 0$ limit. Using a slightly different tight-binding fit to the LDA bands, these authors found that the e'_g bands were shifted below E_F, and that the width of the t_{2g} bands was strongly reduced from 1.5 eV to about 0.5 eV. Thus, while the Fermi surface appears to agree with the ARPES data, the band narrowing is much stronger than experimentally observed. Similar Gutzwiller calculations in the $U \to \infty$, $J = 0$ limit were recently carried out by Shorikov et $al.$ [9], with results similar to those of Ref. [8]. Since the Gutzwiller method replaces the frequency dependent complex self-energy by parameters providing orbital depending energy shifts and band narrowing, it represents an approximation to DMFT. Moreover, for $U \to \infty$, complete orbital polarization is to be expected. Thus, for a meaningful comparison with ARPES data, it is important to extend the Gutzwiller approach to realistic Coulomb and exchange energies appropriate for Co.

The influence of correlations on the electronic properties of hydrated Na$_{0.35}$CoO$_2$ were also investigated by Landron and Lepetit [10] within quantum chemical methods for embedded CoO$_6$ and Co$_2$O$_{10}$ clusters. The crystal field splitting between a_g and e'_g orbitals was found to be $\Delta = 315$ meV, and the Coulomb and exchange energies $U = 4.1$ eV and $J = 0.28$ eV. At present, it is not clear how these parameters, in particular, the large value of Δ, would be modified for larger clusters that are required to describe the electronic properties of the extended system. Slave-boson mean field calculations by Bourgeois et $al.$ [11] based on $\Delta = 315$ meV and $U \to \infty$ revealed a pure a_g Fermi surface and a t_{2g} band width of 0.5 eV, similar to the results of Ref. [8].

To examine the role of Hund exchange contributions not included in the QMC/DMFT calculations, Perroni et $al.$ [12] applied a new multi-band exact diagonalization DMFT scheme to Na$_{0.3}$CoO$_2$. This approach does not suffer from sign problems and includes density-density contributions as well as spin-flip and pair-exchange terms. Also, larger values of U can be handled than via QMC. The result of this study was that in this material there is little difference between Hund and Ising exchange, and that, for $U = 3 \ldots 5$ eV and $J = U/4$, the e'_g pockets were slightly enlarged, in agreement with

the QMC/DMFT results. Also, the band narrowing was found to be roughly 30 %, consistent with the QMC treatment and with the ARPES data.

Most recently, Marianetti *et al.* [13] studied the problem of the e'_g hole pockets in $Na_{0.3}CoO_2$ by applying a new continuous-time QMC/DMFT version that allows to reach larger U and lower temperatures. The single-particle Hamiltonian was the same as in Ref. [8], except for the crystal field splitting $\Delta = E_{a_g} - E_{e'_g}$ that shifts the a_g bands up and the e'_g bands down. For $U = 3 \ldots 5$ eV and $J = 0$, reduced e'_g pockets are found for $\Delta = -10$ meV, and fully suppressed pockets if Δ is increased to $50 \ldots 100$ meV. According to the authors, their results are "in agreement with Ref. [8] and in disagreement with Ref. [5]". Since the DMFT calculations, however, were not done for the same input Hamiltonian and U, J values as those in Refs. [5, 12], the origin of the conflicting trends is presently unknown.

The purpose of this work is to resolve this issue and to analyze the role of the single-particle Hamiltonian $H(k)$ and Coulomb and exchange energies for the charge transfer between t_{2g} bands. In particular, we show that the ED and QMC many-body calculations are in perfect agreement if identical input parameters are employed. On the other hand, the two different versions of $H(k)$ used in Refs. [5, 12] and [8, 13] (below we refer to them as H_1 and H_2, respectively) give rise to a slight, but significant difference in the variation of e'_g occupancy with U: Whereas H_1 yields decreasing e'_g occupancy with increasing U, H_2 gives the opposite trend. We show that these differences are caused by the t_{2g} crystal fields Δ contained H_1 and H_2. The key point, however, is that, for realistic Coulomb and exchange energies, i.e., $U \approx 3 \ldots 5$ eV and $J \approx 0.72$ eV [14], the differences caused by $H(k)$ are small and do not affect the controversy concerning the shape of the Fermi surface. Both versions of $H(k)$ yield the result that, without an additional a_g/e'_g crystal field splitting, Coulomb interactions do not eliminate the e'_g hole pockets. The overall topology of the Fermi surface remains the same as predicted by LDA band theory.

Fig. 1 shows the tight-binding fits to the partially occupied Co $3d$ t_{2g} bands used in Refs. [5, 12] and [8, 13]. The total occupancy is 5.3. The a_g and e'_g occupancies (per spin band) are $n_{a_g} \approx 0.80$ and $n_{e'_g} \approx 0.925$. Although both Hamiltonians give similar energy bands, they differ in a fundamental aspect: The predominant a_g wave function character of the lowest LAPW band along MK [2] is correctly reproduced via H_1, resulting in a van Hove singularity in the a_g density of states near -1.12 eV. In contrast, the two lowest H_2 bands along MK cross, so that this singularity is shifted to -0.84 eV, implying a significant effective narrowing of this subband. The lowest H_2 band at M has e'_g character and gives only a weak step at -1.02 eV in the density of states. Since the influence of Coulomb interactions is highly sensitive to the band width and the distribution of spectral weight within a band, these differences should affect also the correlation induced charge transfer between t_{2g} bands.
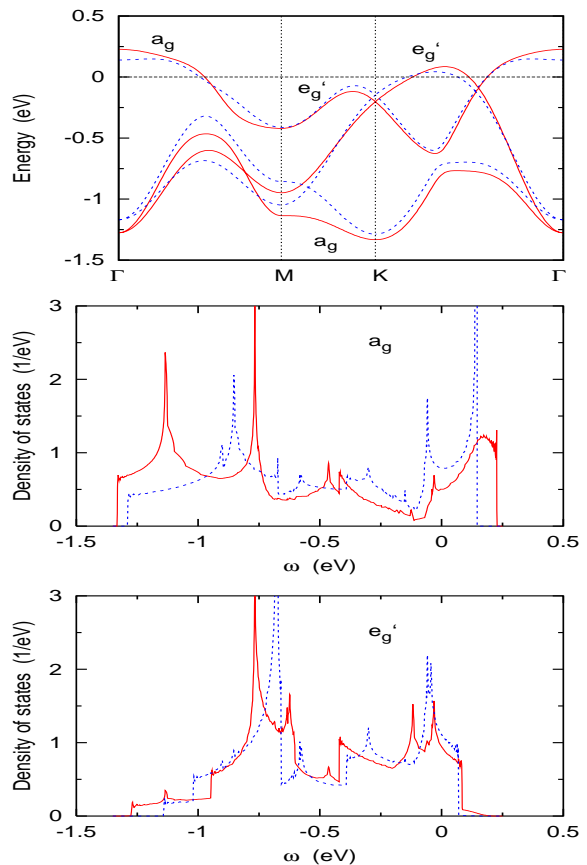

FIG. 1: Upper panel: Tight-binding fits to LDA t_{2g} band structure of $Na_{0.3}CoO_2$ used in Refs. [5, 12] and Refs. [8, 13]. Lower panels: comparison of a_g and e'_g density of states. Solid (red) curves: H_1, dashed (blue) curves: H_2, $E_F = 0$.

The top of the H_2 a_g band at Γ is seen to exhibit a minimum which is absent for H_1 and leads to a pronounced peak in the density of states. This spectral weight is distributed over a slightly wider energy range in the case of H_1. The minimum is caused by interlayer interactions which are absent in H_1 as well as H_2. Moreover, the bulk a_g density of states does not exhibit a sharp peak in this region. Thus, the H_1 a_g density shown in Fig. 1 should be more appropriate than the one derived from H_2.

Despite these differences, near E_F both Hamiltonians yield nearly identical bands. The e'_g bands extend less than 100 meV above E_F, and both models exhibit the a_g / e'_g crossing along ΓK just below E_F. Note that these bands hybridize away from this symmetry direction, i.e., the crossing turns into an increasing hybridization gap as soon as the parallel momentum deviates from ΓK.

We now discuss the correlation induced changes of the t_{2g} bands of $Na_{0.3}CoO_2$ as calculated within DMFT. We had previously demonstrated that, for the Hamiltonian H_1, the QMC and ED results of Refs. [5, 12] are in excellent agreement and that both schemes yield reduced orbital polarization with increasing U. Moreover, this trend was found to be insensitive to the choice of J.

We have applied the ED approach of Ref. [12] to H_2, in order to check its consistency with the QMC formalism used in Ref. [13]. For $U = 3$ eV, $J = 0$, the subband self-energies as a function of Matsubara frequency were found to be in almost quantitative agreement. In view of the inevitable slight numerical differences between these fundamentally different DMFT approaches, the excellent agreement between the ED and QMC results is indeed remarkable. We also point out that both DMFT schemes take proper account of static and dynamical correlations.

The unexpected result of this calculation is that, with H_2 as input, both ED and QMC schemes yield *enhanced* orbital polarization: For $U = 3$ eV, $J = 0$, the subband occupancies are $n_{a_g} = 0.735$, $n_{e'_g} = 0.957$, compared to the LDA values $n_{a_g} = 0.8$, $n_{e'_g} = 0.925$. This charge transfer is opposite to the *reduced* orbital polarization obtained for H_1: $n_{a_g} = 0.825$, $n_{e'_g} = 0.91$.

Fig. 2 shows that similar systematic differences between H_1 and H_2 are found at other values of U, J. To eliminate other sources of possible differences, all results are derived using the ED/DMFT approach of Ref. [12] at $T = 20$ meV. Regardless of the choice of J, H_1 leads to a reduction of $n_{e'_g}$ as a function of U, whereas H_2 yields increasing $n_{e'_g}$. Thus, although the single-particle band structure and density of states derived from H_1 and H_2 look qualitatively similar, these two Hamiltonians lead to a small, but significant difference in the variation of the subband occupancies with Coulomb energy.

To analyze the origin of this unusual behavior we simplify the evaluation of the quasi-particle Green's function

$$G(i\omega_n) = \sum_k [i\omega_n + \mu - H(k) - \Sigma(i\omega_n)]^{-1}, \quad (1)$$

where $\omega_n = (2n+1)\pi/\beta$ are Matsubara frequencies, with $\beta = 1/k_B T$ and temperature T. G, H and Σ are matrices in the t_{2g} basis. Because of the planar hexagonal symmetry, the diagonal elements of G are identical, and so are the off-diagonal elements. The same applies to Σ. In the a_g, e'_g basis, these quantities become diagonal, with elements $G_a = G_{11} + 2G_{12}$ and $G_e = G_{11} - G_{12}$, and analogous expressions for $\Sigma_{a,e}$. In this basis, the Green's functions can be approximately written as

$$G_i(i\omega_n) = \int d\omega \rho_i(\omega)[i\omega_n + \mu - \omega - \Sigma_i(i\omega_n)]^{-1}, \quad (2)$$

where $\rho_i(\omega)$ are the a_g and e'_g density of states components shown in Fig. 1. We have checked that Eq. (2) yields self-consistent DMFT solutions nearly identical to the ones derived from Eq. (1). Thus, the different solutions obtained for H_1 and H_2 are directly related to the different shapes of the respective density of states distributions. As is evident from Fig. 1, the e'_g densities are quite similar for both Hamiltonians. Indeed, replacing one by the other does not alter the trends for the charge transfer shown in Fig. 2. It is clear, therefore, that the different shapes of the a_g density of states are the source of the opposite orbital polarization found for H_1 and H_2.
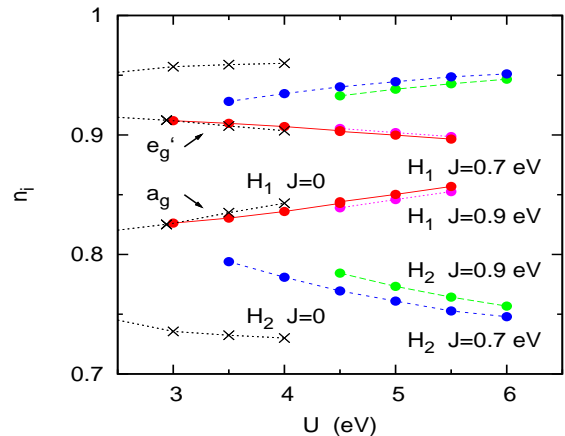

FIG. 2: Subband occupancies as a function of U for fixed J derived within ED/DMFT for $T = 20$ meV. Solid (red) curves: H_1, $J = 0.7$ eV; dotted (magenta) curves: H_1, $J = 0.9$ eV; dashed (blue) curves: H_2, $J = 0.7$ eV; long-dashed (green) curves: H_2, $J = 0.9$ eV. For comparison, some results for $J = 0$ are also shown (crosses).

As pointed out above, the fact that the lowest H_2 bands cross along MK leads to an upward shift of the lowest a_g van Hove singularity by about 0.3 eV. One can simulate this redistribution of spectral weight by reducing the a_g density of H_1 in the range $\omega < -0.7$ eV and amplifying it in the region -0.7 eV$< \omega < 0$, such that the occupied weight remains 0.8. This deformation is sufficient to reverse the trend of $n_i(U)$ and give rise to a weak enhancement of orbital polarization.

Evidently, the upward shift of spectral weight caused by the band crossing along MK implies a relative shift of $3d$ energy levels. In the case of H_1, the centroids of the a_g and e'_g density of states are $E_{a_g} = -0.624$ eV and $E_{e'_g} = -0.491$ eV, where $\Delta = E_{a_g} - E_{e'_g} = -133$ meV is the t_{2g} crystal field splitting. In the tight-binding fit, Δ was varied along with the hopping parameters, in order to achieve the optimum representation of the LAPW bands throughout the Brillouin Zone [5]. Clearly, its value reflects the electronic structure of the extended system. In the case of H_2, the splitting was chosen as $\Delta = -10$ meV, and only the hopping parameters were fitted [8]. The a_g and e'_g centroids therefore nearly coincide: $E_{a_g} = -0.489$ eV and $E_{e'_g} = -0.479$ eV. Note that, in both cases, $E_{a_g} < E_{e'_g}$ despite $n_{a_g} < n_{e'_g}$.

As a result of these different level splittings, correlations lead to an intriguing reversal of interorbital charge transfer: For H_1 with $\Delta = -133$ meV, the large a_g/e'_g splitting is enhanced and gives rise to a gradual filling of the a_g band with increasing U. Since, at small U, the a_g occupancy is lower than the e'_g occupancy, this charge transfer amounts to an initial reduction of orbital polarization. (At larger U, n_{a_g} might become larger than $n_{e'_g}$, so that the same correlation induced $e'_g \rightarrow a_g$ charge transfer eventually could turn into enhanced orbital polarization.) In contrast, the small crystal field included

in H_2, $\Delta = -10$ meV, is too weak to enforce a correlation induced downward shift of the a_g band. Thus, the charge transfer is dominated by the larger e'_g occupancy, giving enhanced orbital polarization even at small U.

Since H_1 provides the more accurate fit to the LAPW bands, the correlation induced reduction of orbital polarization in the range of reasonable values of U and J should be more realistic than the opposite trend obtained for H_2. Thus, as argued in Refs. [5, 12], correlations slightly enhance the e'_g hole pockets of $Na_{0.3}CoO_2$. We emphasize, however, that, according to Fig. 2, the opposite charge transfer obtained for H_2 is not large enough to push the e'_g bands below E_F.

As pointed out in Ref. [13], a large positive crystal field can enhance orbital polarization, so that, in combination with local Coulomb interactions, the e'_g hole pockets disappear [15]. If we assume the ARPES data to be correct, the crucial question then concerns the physical origin of such a crystal field. Evidently, it is not related to on-site Coulomb interactions in the spirit of a single-site DMFT. Non-local effects stemming from the momentum dependence of the self-energy have not yet been explored and could be studied by using a cluster extension of the DMFT. Na disorder was shown to eliminate the pockets at large Na concentrations near $x = 0.7$ [16, 17], but is believed to be too weak to have a significant effect on the Fermi surface near $x = 0.3$. Surface effects which have played an important role in ARPES data on other perovskites, such as $Ca_{2-x}Sr_xRuO_4$ and $Ca_{1-x}Sr_xVO_3$, should also be investigated, in particular, the effect of Na induced states on the first layer. Moreover, possible structural distortions, such as intra-planar buckling, and their connection to the opening of the a_g/e'_g hybridization gap along ΓK should be explored.

We finally mention that, as emphasized in Ref. [13], the e'_g hole pockets are also important for the understanding of the heat capacity of $Na_{0.3}CoO_2$. At present, the experimental value, $\gamma \approx 12 \ldots 16$ mJ/molCoK^2, is difficult to reconcile with the LDA result, ~ 14 mJ/molCoK^2, and an effective mass enhancement of about 2, as derived within the DMFT studies discussed above. For a more detailed analysis of this quantity it might be necessary to relax the pinning condition implied by the single-site approximation and allow for non-local effects.

In summary, we have resolved the puzzling discrepancies between DMFT results for the correlation induced a_g/e'_g charge transfer in $Na_{0.3}CoO_2$. For identical input quantities, ED and QMC impurity treatments are in excellent agreement. Surprisingly, however, slight differences among the tight-binding Hamiltonians lead to increasing or decreasing orbital polarization. This reversal of subband occupancies as a function of U underlines the importance of using a high-quality single-particle basis as input in the many-body calculation. In the present system, for realistic Coulomb and exchange energies, the differences resulting from these opposite trends are small, i.e., Coulomb interactions do not fill the e'_g hole pockets. The topology of the Fermi surface of $Na_{0.3}CoO_2$ therefore remains the same as predicted by LDA band theory.

We hope that these results encourage further experimental work to study in more detail the geometrical and electronic structure of this fascinating material.

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